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NITRATE AND SULPHATE DETERMINATIONS IN URANIUM PROCESS SOLUTIONS BY ION CHROMATOGRAPHY

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Analytical Methodology

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MICROMEDIA

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ABSTRACT

The Division of Nuclear Fuel Cycle of the International Atomic energy Agency requested the participation of CANMET in the preparation of a manual of analytical methods for the uranium industry. The staff of the Chemical Laboratory has responded to this request and will issue several reports describing current methodology and laboratory practice. This report describes the chromatographic determinations of nitrate and sulphate in uranium process samples.

Keywords: Uranium process solutions, nitrate, sulphate, ion chromatography

LE NITRATE ET LE SULFATE DANS DES SOLUTIONS DE TRAITEMENT
DE L'URANIUM PAR CHROMATOGRAPHIE par ÉCHANGE D'IONS

par

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RESUME

La division du cycle du combustible nucléaire de l'Agence internationale de l'énergie atomique a demandé au CANMET de participer à la préparation d'un manuel de méthodes analytiques pour l'industrie de l'uranium. Le personnel du Laboratoire de chimie a répondu à cette demande et produira plusieurs rapports décrivant les méthodes et les techniques de laboratoire actuellement utilisées. Le présent rapport décrit le dosage chromatographique du nitrate et du sulfate dans des échantillons de traitement de l'uranium.

Mots-clés: solutions de traiteent de l'uranium, nitrate, sulfate,
chromatographie par échange d'ions

INTRODUCTION

The procedures described are applicable to samples from uranium process circuits containing sulphate and nitrate ions. Two ion chromatographic (I.C.) separation techniques using conductivity detection are described; single column I.C., and suppressed I.C.

A brief summary of the methods follows. A filtered aliquot of sample is injected onto an anion exchange column. The sample is pumped through the separation column by an ionic mobile phase i.e. the eluent. Ions are separated based on their affinity for the exchange sites on the column. In the single column technique the separated anions to be measured are pumped directly into a conductivity detector. In suppressed I.C. the ions, after leaving the separator column, go through a membrane suppressor that contains cation exchange resin in the hydrogen form. This reduces the background conductivity of the eluent. The detection limits for the suppressed I.C. is 2 to 3 times lower than for single column I.C., but with single column technique a choice of eluents is available. This allows the relative retention times to be changed and thereby reduces interference from extraneous anions.

Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve produced from known standards. These procedures allow the determination of nitrate and sulphate in the ppm range.

INTERFERENCE

If one of the sample components is present at very high levels, it may interfere by causing a very large peak on the chromatogram which masks other peaks of interest. This type of interference is normally minimized by dilution of the sample. If chloride and fluoride are not to be determined, then interference due to high levels of organic acids and alkali ions will not be a problem.

EQUIPMENT

Chromatographic System. The system consists of a pump for delivering the eluent, an injector valve with a 50- μ L or 100 μ L sample loop, a conductivity detector, and a recorder or an integrator to measure area under the chromatogram. A chromatographic system for suppressed I.C. is available from Dionix Corp., 1228 Titan Way, Sunnyvale California, 94086, U.S.A. A single column I.C. system is available from Waters, 34 Maple Street, Milford, M.A., 01757, U.S.A.

PRECOLUMN

A short length column of similar material to the separator column and placed before the separator column is recommended to protect the main column from being contaminated by particulates and irreversible adsorbing constituents.

SEPARATOR COLUMNS

A styrene-divinylbenzene based low capacity pellicular anion exchange column (Dionex PIN 35311) for suppressed I.C. A hydrophilic polymethacrylate gel anion exchange column (Waters IC Pak-A PN07355) for single column I.C.

SUPPRESSOR COLUMN

A column or membrane that is a high capacity cation exchanger and is capable of converting the eluent and separated anions to their respective acid forms.

REAGENTS

Reagent grade chemicals are used in all preparations. All solutions are prepared from distilled water purified with a Mille-Q (Millipore) System.

ELUENT (FOR SUPPRESSED IC)

Dissolve 1.0080 g of sodium bicarbonate (0.003 M NaHCO_3) and 1.0176 g of sodium carbonate ($0.0024 \text{ M Na}_2\text{CO}_3$) in water and dilute to 1 litre with water. Dilute $250 \pm 1 \text{ mL}$ to 1 L, filter through a $0.45 \mu\text{m}$ filter, store stock in refrigerator and make up eluent fresh each day.

ELUENT (SINGLE COLUMN I.C.)

Gluconate/borate eluent - 1.2 M potassium gluconate, 1.3 M boric acid. Dissolve 0.30 g of potassium gluconate, 0.50 g of sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{ H}_2\text{O}$), 0.50 g of boric acid (H_3BO_3) and 5.0 g of glycerin in 500 mL of water. Transfer to a 1 litre flask. Mix together 120 mL of acetone and 30 mL of n-butyl alcohol. Add this mixture to the contents of the 1 litre flask and dilute with H_2O . Check pH to be 8.4 to 8.5. Filter through a $0.45 \mu\text{m}$ filter.

ANION STOCK SOLUTIONS

Nitrate ($1 \text{ mL} = 1.00 \text{ mg of NO}_3^-$) - Dry ca. 2 g sodium nitrate (NaNO_3) at 105°C for 24 h. Dissolve 1.3707 g of the dried salt in water and dilute to 1 L with H_2O .

Sulphate ($1 \text{ mL} = 1.00 \text{ mg of SO}_4^{2-}$) - Dry sodium sulphate (Na_2SO_4) for 1 h. at 105°C and cool in desiccator. Dissolve 1.4790 g of the dried salt in water and dilute to 1L with water.

ANION WORKING STANDARDS

Prepare three working standard solutions to contain concentration of anions as shown in Table 1. Prepare a high-range standard solution by transferring 10.0 mL of nitrate stock standard, and 20.0 mL of sulphate stock standard to a 250 mL flask and dilute with appropriate eluent.

Prepare an intermediate range standard solution by diluting 10.0 mL of the high-range standard solution to 100 mL with eluent.

Prepare the low-range standard solution by diluting 10.0 mL of the intermediate-range standard solution to 100 mL with eluent.

Table 1 - Concentration of Standard Solution for Calibration

Anion	High std mg/L	Intermediate std mg/L	Low std mg/L
NO_3^-	40	4	0.4
$\text{SO}_4^{=}$	80	8	0.8

CALIBRATION

DETERMINATION OF RETENTION TIMES

The retention time for each anion is determined by injecting a standard solution containing only the anion of interest and noting the time required for a peak to appear on the chromatogram. Although retention times may vary from one column to another and are effected by temperature and eluent flow rates, the elution order of the anions is always NO_3^- followed by $\text{SO}_4^{=}$.

PREPARATION OF CALIBRATION CURVES

Analyze the blank and each of the prepared working standards in accordance with the procedure. Prepare calibration curves for each anion by plotting on linear graph paper peak height of peak area versus the concentration of the anion.

PROCEDURE

Equilibrate the system by pumping eluent through the columns until a stable baseline is obtained, ca. 30 min. The detector ranges are variable; normal operating ranges are from 3 to 100 μ S/cm full scale. The range setting required for analysis will depend on the concentration of anions in the sample and should be chosen accordingly. Load the sample loop by injecting ca. 1 mL of sample into the entry port using a 3 mL plastic syringe. Inject the sample onto the column and record the ion chromatogram. To identify peaks of interest in a complex sample, inject a sample containing the addition of the anion of interest.

CALCULATIONS

Refer the peak height or area noted for the anions to the appropriate calibration curves to determine the anion concentration in $\mu\text{g/mL}$.

$$\text{Anion concentration mg/L} = A \times F$$

where:

A = μg per mL read from the appropriate calibration curve.

F = dilution factor.

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